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# Investigation of adsorption efficiency of $Cu^{2+}$ and $Zn^{2+}$ by red soil and activated bentonite from acid copper mine drainage

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## ABSTRACT

Heavy metals can be transmitted to living creatures and ultimately to humans through various ecosystems due to their accumulative properties. The entry of these compounds through acid mine drainage into the water, soil, and agricultural products has created a condition that is considered always a threat for human health. The research was carried out in order to investigate the removal of $Cu^{2+}$ and $Zn^{2+}$ by red soil and activated bentonite from acid copper mine drainage in Rafsanjan. Variables examined in this study were temperature, particle size, contact time, pH, and adsorbent concentration. Both adsorbents were characterized using X-ray fluorescence and Fourier transform infrared. The $Cu^{2+}$ and $Zn^{2+}$ concentrations of samples were determined using flame atomic absorption spectroscopy after the adsorbents were added. The results showed that increases in contact time from 5 to 45 min had a notable effect on the removal process. The $Cu^{2+}$ removal rates by both adsorbents were higher than those of $Zn^{2+}$. The current study showed that the process of adsorption of $Cu^{2+}$ and $Zn^{2+}$ ions by natural soils is a thermal reaction, and adsorption capacity and equilibrium increase with increasing temperature. With reducing adsorbent particle size from the range of 2–6.7 mm to the range of 0.5–0.8 mm, the removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ was reduced on average by 13% using activated bentonite and red soil. The results indicated that the $Cu^{2+}$ and $Zn^{2+}$ of acid copper mine drainage could be reduced using activated bentonite and red soil as low-cost and available adsorbents. Results indicated that Freundlich adsorption isotherm was the best model for the metal ion adsorption onto the activated bentonite and red soil with higher $R^2$. The kinetic studies revealed that the adsorption process followed the pseudo-second-order kinetics model. The decrease of the adsorption efficiency in the real sample was notable compared with the synthetic sample, and this reduction was bigger for zinc metal. The results indicated that the activated bentonite and red soil achieved acceptable efficiency in removing copper and zinc metals from the acid copper mine drainage.

*Keywords:* Acid mine drainage; Bentonite; Heavy metals; Red soil

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## 1. Introduction

Mining causes the pollution of water, soil, and plants not only during exploitation but also after the mines are closed. The environment around the mine can be affected by mining-related pollution, such as heavy metals [1]. Most of these metals have high solubility in water and can cause the pollution of both surface and groundwater and ultimately the soil [2]. Sulfide-rich wastes pollute the environment with heavy metals [3]. The transfer of heavy metals to soil and water increases the number of hazardous materials in living tissues, including the human body. The threat related to heavy metals lies in their mobility, bioavailability, and geochemical forms. Solubility in water and changeable forms facilitate the movement of pollutants and make them accessible to living organisms [4]. Acidic effluent with low pH values contains high concentrations of iron, manganese, sulfate ions, and other pollutants, and when discharged to unpolluted water, it significantly affects its quality [5]. In areas where surface water and groundwater are polluted with acid mine drainage, it is very difficult and costly to treat the water for drinking and industrial purposes [6]. Most acid mine drainages from copper mining include low pH, high total dissolved solids, acidity, and sulfate, and high concentrations of soluble metals [7]. Exposure to Cu leads to necrosis in the liver, kidney damage, mucosal irritation, widespread capillary damage, depression, weakness, lethargy, anorexia, gastrointestinal irritation, and lung cancer [8]. $Zn^{2+}$ being in the list of priority pollutants proposed by Environmental Protection Agency gives rise to serious poisoning cases. The main symptoms of zinc poisoning are dehydration, electrolyte imbalance, stomachache, nausea, dizziness, and in coordination in muscles [9]. Treatment methods of acid mine drainage are generally divided into two categories: active and passive processes. Active processes utilize alkaline materials such as lime, limestone, hydrated lime, NaOH, and caustic soda. Other active processes include aeration, acidity reduction, and metal precipitation. Passive processes are chemical and biological processes that occur naturally in a controlled environment [10]. The conventional treatment methods for acid mine drainage are very expensive, and the cost of maintaining and operating these methods are problematic [11]. Adsorption is the relatively suitable technique which can be used to reduce a load of heavy metals in the wastewater, since adsorbing materials have the metal-binding capacity. The major advantage of adsorption over conventional treatment includes low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of sorbent, and possibility of metal recovery [12]. Recently, the utilization of alternative materials such as adsorbents, despite their lower efficiency, has received greater attention due to their lower costs [13]. Natural clay is evaluated as an appropriate adsorbent due to its low cost and high removal efficiency. Their sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives the capability to attract metal ions [9]. Bentonite is classed as natural clay of layered phyllosilicates, composed of alternating octahedral and tetrahedral sheets in the ratio of 2:1. The structure, chemical composition, exchangeable ion type, and small crystal size contribute to the unique property of bentonite including a large chemically active surface area, high cation exchange capacity, and high porosity. Also, bentonite is easily available all over the world [14]. Red soils are formed due to weathering of igneous rocks. They are deficient in nutrients and humus and have low water-holding capacity. The red color is mainly due to the presence of iron oxides. Red soil possesses lower strength compared with other soils due to its porous and friable structure [15].

In Iran, Esmaeili et al. [16] studied the process of adsorbing copper and nickel from aqueous solutions with a type of volcanic ash. Feng et al. [17] investigated the removal of pollutant heavy metals from mine drainage in South Africa using the side products of slag. Gitari et al. [18] surveyed the removal of heavy metals from the acid waste of mine by volatile ash in South Africa. In Greece, Stylianou et al. [19] investigated the removal of $Cu^{2+}$ from aqueous solutions with zeolite and vermiculite adsorbents. In England, Rios et al. [20] studied the removal of heavy metals from acid mine drainage using volcanic ash, enamel bricks, and synthetic zeolite. Calvo et al. [21] investigated the removal of lead, copper, and zinc from acidic waters using natural zeolite; their study resulted in an economic, effective, and environment-friendly removal method. In Iran, Malakootian et al. [22] surveyed the removal of heavy metals from wastewater of the paint industry using lightweight expanded clay aggregate mineral adsorbent. Egashira et al. [23] investigated the removal of heavy metals from the leachates of mines in the Czech Republic using Mongolian natural zeolite. Tamoto et al. [24] studied the effects of adsorption on reducing arsenic in mine drainage using volcanic ash. In China, Fan et al. [3] investigated the removal of heavy metals from the acid drainage of rubbish pyrite using calcium carbonate. Qian et al. [25] studied the treatment of acid mine drainage using natural and synthetic materials in Australia.

According to literature, no study has been done on $Cu^{2+}$ and $Zn^{2+}$ adsorption using activated bentonite and red soil on Sarcheshmeh acid copper mine drainage. The process of removing heavy metals from the real sample was carried out. Due to the presence of anions, cations, and other intrusive compounds, the process of removal was more complex and different. Modification of bentonite was carried out in order to increase the adsorption capacity. Comparison of heavy metal adsorption has been made between activated bentonite and red soil.

## 2. Experiments

### 2.1. Materials and methods

Batch experiments were conducted in flasks with a volume of 300 mL, mixing speed of 150 rpm, and temperature of 27°C ± 1°C. Standard solutions of copper and zinc were prepared by dissolving certain amounts of copper and zinc nitrate salts by adding a few drops of nitric acid and then distilled water. Solution pH was calibrated by nitrate and nitric acid, and high-purity sodium hydroxide was purchased from Merck, Germany. After adding the required amount of adsorbent to each sample, the adsorbates, $Cu^{2+}$ and $Zn^{2+}$, were thoroughly mixed using a magnetic stirrer at a speed of 150 rpm. Next, the samples were passed through filter paper with a pore size of 0.45 μm. Sample concentrations of $Cu^{2+}$ and $Zn^{2+}$ were determined using flame atomic absorption spectroscopy, Shimadzu-AA-670 model [16,26].

The adsorption capacity and removal percentage of $Cu^{2+}$ and $Zn^{2+}$ onto adsorbent were obtained according to Eqs. (1) and (2):

$$q_e = \left(\left(C_0 - C_e\right)m\right) \times v \tag{1}$$

$$\%R = \left[\frac{\left(C_0 - C_e\right)}{C_0}\right] \times 100 \tag{2}$$

where $q_e$ is the adsorption capacity of the adsorbent for the metal solution (mg/g), $C_0$ is the initial concentration of the metal solution (mg/L), $C_e$ is the equilibrium concentration in the metal solution (mg/L), $m$ is the mass of the adsorbent (g), $V$ (L) is the volume of the metal solution, and $R$ (%) represents the removal percentage of metal on adsorbent [27]. The priority of uptake of heavy metals from acid mine drainage with montmorillonite base adsorbents is as below [28]:

Cd = Zn > Ni

For mineral adsorbents, it is

Pb > Cu > Zn >Cd

### 2.2. Preparation of adsorbent

The bentonite and red soil are two types of mineral soils that were collected from mines in Kerman. The collected adsorbents were initially crushed and then dried at laboratory temperature and exposed to airflow for 2 weeks. The red clays have a reddish or reddish-brown color, and vertical features are more prominent in the older, reddest palaeosols. The reddish color of soils and palaeosols is attributed to hematite, goethite, maghemite, and/or “amorphous” Fe oxides formed pedogenically or during early diagenesis as a result of dehydration or oxidation of Fe oxyhydroxides or may be inherited from the parent material. Generally, red clay displays a prismatic structure with slickensides, stress surfaces, and brown and yellowish spots. Calcretes, 3–5 cm in diameter, occur in the lower part of the red clay. Black Fe–Mn stains are generally abundant throughout the entire red clay unit [29]. The bentonite was modified by treating it with HCl under favorable conditions of high temperature. Acid activation helps increase the sorption sites, vary the surface area, enhance thermal stability, and enhance adsorption capacity [14]. Particles were selected from 50 to 100 meshes for testing.

### 2.3. Characterization methods

To perform elemental analysis and determine the percentage of available elements in materials, the X-ray fluorescence (XRF) test was employed. The chemical composition of the bentonite and red soil is determined using the XRF spectrometer, PW 4110/00 Venus100 minilab model. The Fourier transform infrared (FTIR) spectra of red soil and activated bentonite were taken by the use of the FTIR spectrophotometer (TENSOR 27-BRUKER). FTIR spectra of the samples were recorded in the region 4,000–200 $cm^{-1}$.

### 2.4. Kinetic adsorption

An important step for the understanding of adsorption mechanisms and valuation of adsorbent performance is adsorption kinetics. Two models that are widely used to analyze the solid-liquid adsorption are pseudo-first-order and pseudo-second-order kinetics [30]. Adsorbate contact time, the reactor dimensions, and predicting the rate at which adsorption takes place are probably the most important factors in the adsorption system design that are controlled by the system’s kinetics [31]. The kinetic data were treated with the first-order model which is the earliest known one describing the adsorption rate based on the adsorption capacity.

The linearized form of the pseudo-first-order equation of Lagergren is generally expressed as follows:

$$\log\left[q_e - q_t\right] = \log\left[q_e\right] - \left[\frac{k_1}{2.303}\right]t \tag{3}$$

where $q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$, respectively (mg/g). $k_1$ is the rate constant of pseudo-first-order adsorption. The plot of $\log(q_e – q_t)$ vs. $t$ should give a linear relationship; $k_1$ and $q_e$ can be calculated from the slope and intercept of the plot, respectively. The pseudo-second-order kinetic model is represented by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{kq_e} + \frac{1}{q_e t} \tag{4}$$

where $q_e$, $q_t$, and $t$ have the same meaning as explained above, $k_2$ is the overall rate constant of pseudo-second-order sorption (g/mg/min). If pseudo-second-order kinetics is applicable, the plot of $t/q_t$ against $t$ of Eq. (3) should give a linear relationship; $q_e$ and $k_2$ can be determined from the slope and intercept of the plot. The initial sorption rate can be obtained from the pseudo-second-order linear plots as $q_t/t$ approaches zero [32].

For adsorption system following the pseudo-second-order kinetics, the adsorbate was assumed to get adsorbed onto two surface sites. Thus, the sorption kinetics following pseudo-second-order kinetics can be represented as Eq. (5):

$$\frac{d_q}{d_t} = k_2\left(q_e - q_1\right)^2 \tag{5}$$

where $k_2$ is the rate constant of pseudo-second-order adsorption (g/µg/h), $q_e$ is the amount of solute adsorbed at equilibrium (µg/g), and $q_t$ is the amount of solute adsorbed at time $t$ (µg/g). Integrating Eq. (5) for boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives [33]

$$q_t = \frac{q_e^2 k_2 t_e}{1} + k_2 q_e t \tag{6}$$

### 2.5. Adsorption isotherms

Two isotherm equations were used to determine the Langmuir and Freundlich models:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^{\circ}b}\right) + \left(\frac{C_e}{Q^{\circ}}\right) \tag{7}$$

$$\log\left(q_e\right) = \log\left(K_F\right) + \frac{1}{n}\log\left(C_e\right) \tag{8}$$

where $C_e$ and $q_e$ are equilibrium concentration and equilibrium adsorption capacity (mg/g), $Q°$ is the maximum equilibrium adsorption capacity of metal on the surface of adsorbent (mg/g), and $b$ shows the correlation energy adsorption (L/mg). $K_F$ and $n$ are Freundlich constants; $K_F$ is associated with adsorption capacity (mg/g) (L/mg) $1/n$, and $n$ shows the tendency to adsorb [34].

### 2.6. Real solution

Experiments were carried out on the wastewater from the acid mine drainage of Sarcheshmeh copper mine in Rafsanjan, Kerman, Iran. Composite sampling was done to prepare the real samples from it. At the end of the winter and summer seasons, the composite real sample was taken from the Sarcheshmeh copper mine. Adsorption experiments were performed using synthetic solutions. After determining optimal conditions, tests were performed on wastewater from the acid mine drainage of Sarcheshmeh copper mine in Rafsanjan. Primarily, its quality was determined in terms of Cu, Zn, pH, etc.

### 2.7. Effective parameters on removal efficiency

This study examined the parameters affecting removal efficiencies, including temperature, particle size, contact time, pH, and adsorbent concentration. The values are shown in Table 1.

The experiments were performed using techniques set forth in the Standard Methods for the Examination of Water and Wastewater (21st Ed.) [35].

## 3. Results and discussion

### 3.1. Characterization of adsorbents

The results of the XRF analysis of the sample are shown in Table 2.

Major chemical components of the red soil are MgO (37.8) and $SiO_2$ (36.58); small percentages of calcium, sodium, potassium, iron, and magnesium oxides are also present.

Like red soil, the main chemical components of the activated bentonite are silica oxide (73.36), aluminum oxide (11.39), and calcium oxide (5.4); small percentages of sodium, potassium, iron, magnesium, and oxides are also present.

The FTIR analysis was applied before and after the adsorption to determine the functional groups on the surface of activated bentonite and red soil responsible for adsorption. Results are shown in Figs. 1 and 2. The spectrum displayed the presence of certain functional groups responsible for the adsorption of the metal ions from the aqueous solution and has been discussed extensively [36].

Table 1
Parameters affecting removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ from acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan

| Parameter | Parameter value |
|---|---|
| pH | 2–5 |
| Temperature, °C | 25–35 |
| Contact time, min | 5–120 |
| Particle size, mm | 0.5–0.8 |
| Adsorbent concentration, g/L | 8–24 |

Table 2
Results of XRF* analysis of red soil and activated bentonite

| Chemical composition wt.% | Activated bentonite | Red soil |
|---|---|---|
| $SiO_2$ | 73.36 | 36.58 |
| $Al_2O_3$ | 11.39 | 1.92 |
| $Fe_2O_3$ | 1.23 | 4.53 |
| MgO | 2.3 | 37.8 |
| CaO | 5.4 | 1.84 |
| $Na_2O$ | 0.01 | 0.18 |
| $K_2O$ | 0.056 | 0.24 |
| BaO | – | 0.01 |
| MnO | – | 0.14 |
| $P_2O_5$ | – | 0.01 |
| LOI** | 8.54 | 14.3 |

*XRF: X-ray fluorescence, **LOI: loss of ignition.

The FTIR spectra of activated bentonite were shown while the Si–O bending vibrations were observed at 794.32 cm⁻¹; the Si–O stretching vibration was portended by the adsorption bands at 1,092.77 cm⁻¹. The presence of the Al–O bending vibration was revealed by the band at 620.43–519.94 cm⁻¹ that corresponds to the Al–O–Si skeletal vibrations. As observed in the FTIR spectra of red soil, Si–O–Al and Si–O bending vibrations were observed at 550.31 and 980.69 cm⁻¹, respectively. Previous studies showed that silica and alumina in red soil and activated bentonite were the active sites [37,38]. The FTIR spectral data after adsorption showed noticeable changes in these functional groups of red soil: O–H (3,616.67 and 3,424.14 cm⁻¹), C=C (980.69 cm⁻¹), C–Br (550.3 cm⁻¹), and O–H (3,625.8 and 3,427.39 cm⁻¹); C–N (1,092.77 cm⁻¹) and C=C (725.45 cm⁻¹) as using activated bentonite. It has been proved that carboxylic, hydroxyl, and carbonyl functional groups have an important role in metal adsorption [39].

The FTIR spectra of red soil before and after adsorption are shown in Fig. 1.

The FTIR spectra of activated bentonite before and after adsorption are shown in Fig. 2.

FTIR spectral data of activated bentonite and red soil are shown in Table 3.

### 3.2. Effects of pH solution on removal efficiency

The effects of pH on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using activated bentonite and red soil adsorbents are shown in Fig. 3.

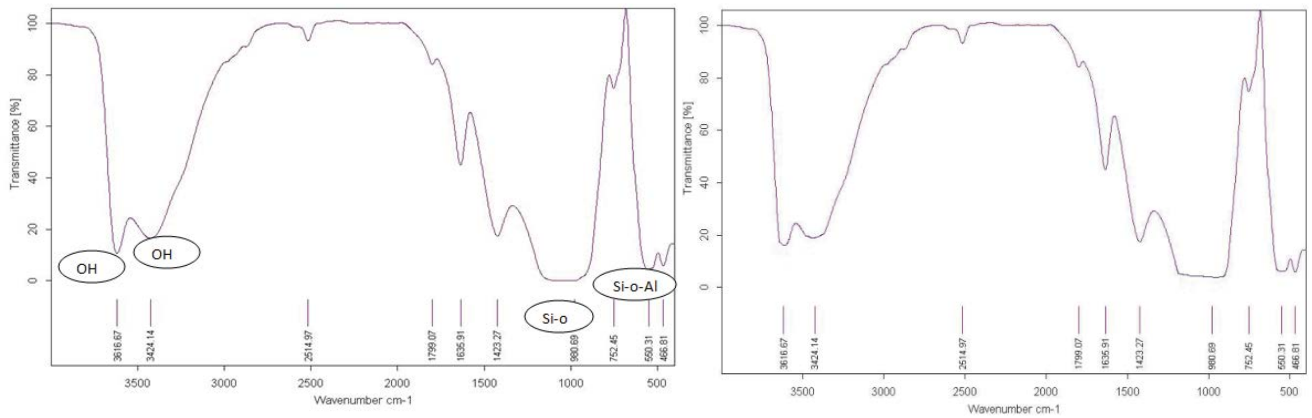
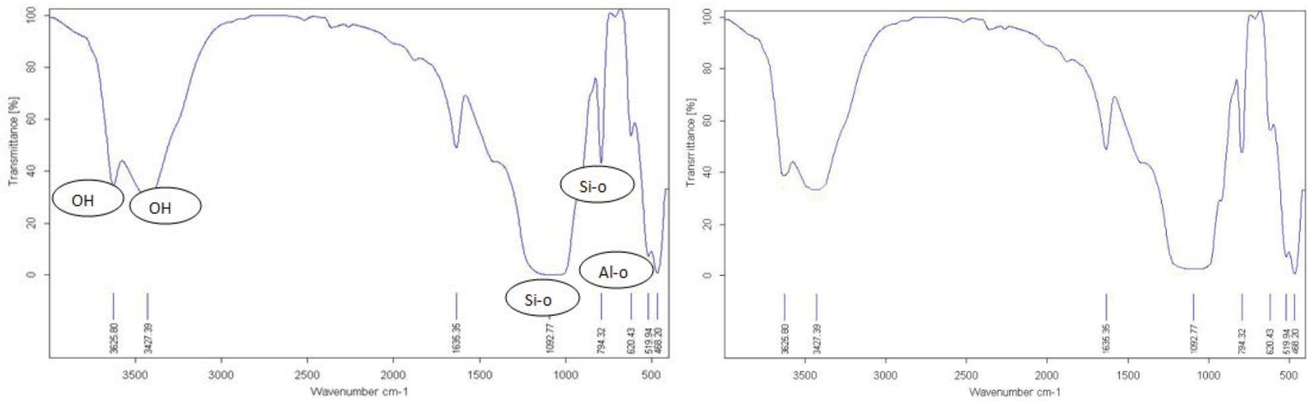


Fig. 1. The Fourier transform infrared spectra of red soil before (a) and after (b) adsorption.



(a) (b)

Fig. 2. The Fourier transform infrared spectra of activated bentonite before (a) and after (b) adsorption.

Table 3
FTIR spectral data of activated bentonite and red soil

| Assignments | Wave number, cm$^{-1}$ | |
|---|---|---|
| | Activated bentonite | Red soil |
| O–H stretching alcohol free | 3,625.8 | – |
| O–H carboxylic acids stretching alcohol free | – | 3,616.67 |
| O–H stretching alcohol bonded intermolecularly | 3,427.39 | 3,424.14 |
| C=C stretching alkene disubstituted (cis) | 1,635.36 | – |
| C=C stretching alkene monosubstituted | – | 1,635.91 |
| C=C bending alkene disubstituted (trans) | – | 980.69 |
| C=C bending alkene disubstituted | – | 725.45 |
| C=O stretching vinyl/phenyl/ester | – | 1,799.07 |
| C–N stretching amine | 1,092.77 | – |
| C–H bending 1,3 disubstituted | 794.32 | – |
| C–H bending alkane methyl group | – | 1,423.27 |
| C–Br stretching halo compound | 620.43–519.94 | 550.31 |
| N–H stretching primary amine | – | 3,424.14 |
| S–H stretching thiol | – | 2,514.97 |
| Bromide-iodide | 468.2 | 466.81 |

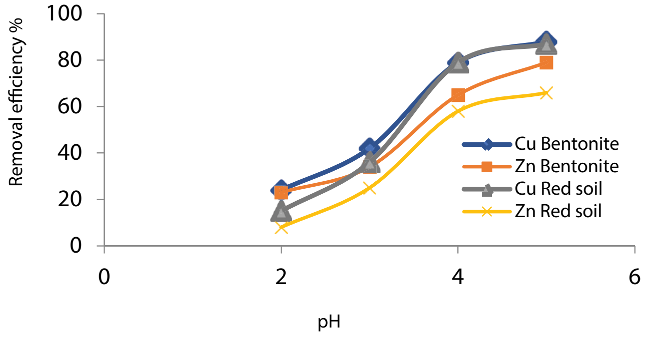


Fig. 3. Effects of pH solution on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (initial concentration of metals = 50 mg/L, particle size = 0.5–0.8 mm, temperature = 25°C, adsorbent concentration = 24 g/L, contact time = 100 min, mixing speed = 150 rpm).

The pH of a solution has an important role in the removal and adsorption of heavy metals, probably because the surface of the adsorbent particles is negatively charged by increasing pH [20]. Due to the solubility of metals in the acidic region, pH was selected in the range of 1–5, until the precipitation of metals minimized [40]. The removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ was increased by increasing pH from 2 to 5. The removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ was increased from 21% and 23% at pH = 2 to 89% and 79% at pH = 5, respectively. The removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ by red soil was increased from 10%–15% and 8% at pH = 2 to 86% and 67% at pH = 5, respectively. Adsorption takes place slightly at lower pH values (up to pH = 3.5–4.0); above this value, adsorption becomes significant and maximized at pH = 5 for both ions ($Cu^{2+}$ and $Zn^{2+}$). The $Cu^{2+}$ and $Zn^{2+}$ begin to hydrolyze and precipitate at higher pH; therefore, they are not involved in adsorption process [41]. $H^+$ ions were adsorbed on the red soil and bentonite surface at low pH values, and the net positive charge resulted in a strong gravitation for negatively charged ions; on the other hand, however, the $OH^-$concentration increased on the adsorbent surface that more free surface was created for the negatively charged ions resulting in the increase of removal efficiency [42]. At low initial pH, the adsorption capacities for two adsorbents are insignificant, and when it increases from 2 to 4, sharp increases of adsorption capacities are observed.

In the adsorption process, pH change was observed as shown in Fig. 4. As time passes, the pH of the solution increased by using both sorbents. Red soil showed a more tangible increase in the pH of the solution. The pH of the aqueous solution increased within 30 min when red soil and activated bentonite were used, while the pH of the solution increased slightly from 5.4 to 6, 6.3 and 6.6, and 6.1 to 6.4 and 6.7, respectively. After 40 min, the pH value obtains a balanced value. The pH change might be due to the dissociation of ionic functional groups, precipitation, and ion exchange process. When the solution had a pH > 6.0, the solution of $Cu^{2+}$ and $Zn^{2+}$ gradually formed $M(OH)_2$ precipitate. The OH ions cause an increase in the pH of the solution. On the other hand, the metal ions can react with $OH^-$ to form precipitates [43].

### *3.3. Effects of adsorbent concentration on removal efficiency*

The effects of adsorbent concentration on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using the adsorbents are shown in Fig. 5.

Results showed that the $Cu^{2+}$ and $Zn^{2+}$ removal efficiency was directly related to changes in the solute concentration and achieved removal rates of 86% and 77% for $Cu^{2+}$ and $Zn^{2+}$, respectively. With increasing concentrations of bentonite to 24 g/L, the removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ was increased. By increasing red soil concentration, from 8 to 20 g/L, removal efficiency was increased. Increases in the adsorbent concentration also increased the removal efficiency of heavy metals from the solution; however, from 20 g/L and above, the removal efficiency almost reached equilibrium. Increasing the concentration of activated bentonite up to 24 g/L increased the $Cu^{2+}$ and $Zn^{2+}$ removal efficiency; maximum adsorption was up to 20 g/L. Perhaps, the reason for this process is that as the number of adsorption sites per unit of mass of an absorbent should be constant, Independence of the total adsorbent mass, the number of accessible sites as the effective surface area is presumably to decrease, as increasing the adsorbent dose in a fixed volume reduces [44]. Similar results have been reported in studies by Arias and Sen [45].

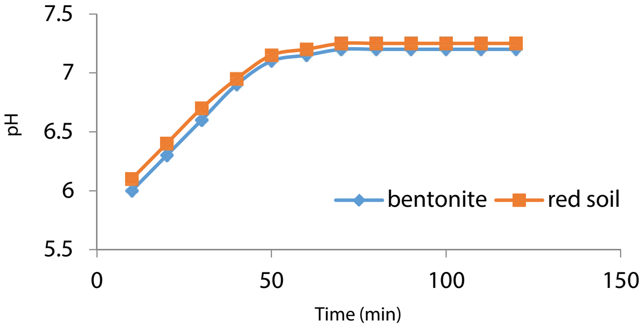


Fig. 4. pH change in $Cu^{2+}$ and $Zn^{2+}$ adsorption process using red soil and activated bentonite from acid mine drainage from copper mining.

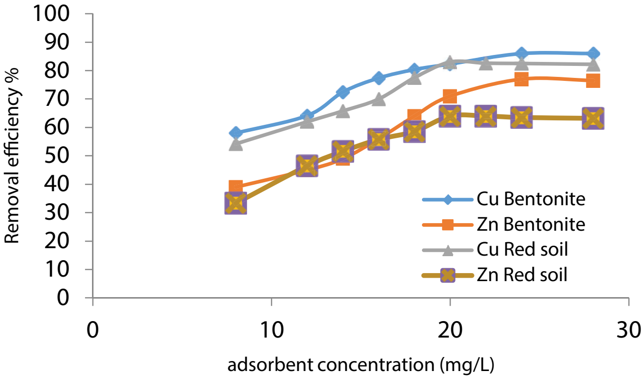


Fig. 5. Effects of adsorbent concentration on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (initial concentration of metals = 50 mg/L, particle size = 0.5–0.8 mm, temperature = 25°C, pH = 5, contact time = 100 min, mixing speed = 150 rpm).

### *3.4. Effects of adsorbent particle size on removal efficiency*

The effects of adsorbent particle size on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using activated bentonite and red soil adsorbents are shown in Fig. 6.

The results of this study showed that reducing the adsorbent particle size from the range of 2–6.7 mm to the range of 0.5–0.8 mm increased the removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ about 13%. The results of this research confirmed that adsorbent particles that are smaller in diameter have higher adsorption power [19]. Reducing particle size causes an increase in the effective surface of the adsorbent and increases removal efficiency at the outer surface of the adsorbent particles. As a result, reducing the particle size increases the probability of penetration by metal ions from the outer surface to the internal cavity. In the large particle, some factors such as mass transfer resistance and blockage of some of the penetration path reduce removal efficiency [46]. Concerning the use of the adsorbent particle size of 2–6.7 mm, the diffusion resistance to mass transfer is higher, and most of the internal surface of the particles may not be used for adsorption, and hence, the removal efficiency is reduced [47]. The breaking of big particle leads to open small cracks and channels on the particle surface that resulted in more access to better diffusion of metal ions into the activated bentonite and red soil [48]. Similar results have been reported by Haibibuxiyili et al. [26] for the removal of some heavy metals onto mechanically activated fly ash and Bhattacharyya et al. [49] for soil properties affecting adsorption.

### *3.5. Effects of contact time on removal efficiency*

The effects of contact time on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using activated bentonite and red soil adsorbents are shown in Fig. 7.

The maximum removal efficiency of $Cu^{2+}$ using red soil was obtained in the initial 20 min. The best contact time for a 14% increase in removal efficiency was 30 min. The best time for the adsorption of $Zn^{2+}$ by red soil was 80 min. Then, with increasing time, the amount of adsorption persisted. This may be due to the saturation of the adsorbent surface with $Cu^{2+}$ and $Zn^{2+}$, which occurred because of the adsorption and desorption [50]. With activated bentonite, increasing contact time increased the removal efficiency of both $Cu^{2+}$ and $Zn^{2+}$. Maximum adsorption of $Cu^{2+}$ and $Zn^{2+}$ ions was achieved at 100 min. In research conducted by Gitari et al. [18] on the removal of heavy metals from acid mine drainage by volcanic ash, the equilibrium time was reported to be between 90 and 360 min. In other research performed by Sen et al. [51] on the removal of copper and nickel metal ions from aqueous solutions by the kaolinite, the equilibrium time was reported to be 4 h. In a research conducted by Esmaeili et al. [16] on the removal of copper and nickel metal ions from aqueous solutions by pumice, the equilibrium time was reported to be 10 min.

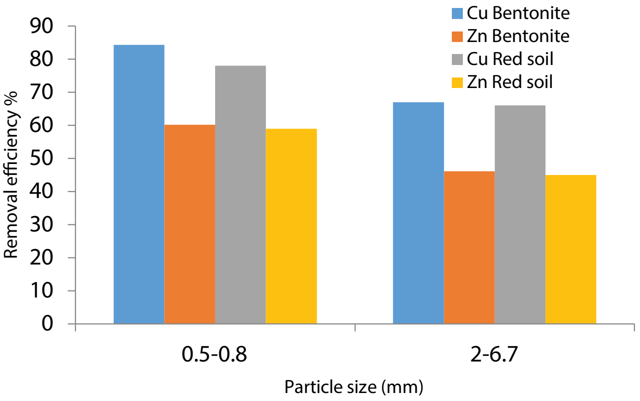


Fig. 6. Effects of adsorbent particle size on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (initial concentration of metals = 50 mg/L, adsorbent concentration = 24 g/L, temperature = 25°C, pH = 5, contact time = 100 min, mixing speed = 150 rpm).

### *3.6. Effect of temperature on removal efficiency*

The effects of temperature on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using activated bentonite and red soil adsorbents are shown in Fig. 8.

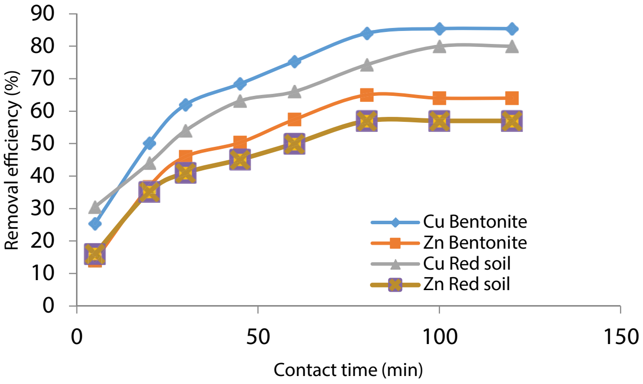


Fig. 7. Effects of contact time on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (initial concentration of metals = 50 mg/L, adsorbent concentration = 24 g/L, temperature = 25°C, pH = 5, particle size = 0.5–0.8 mm, mixing speed = 150 rpm).

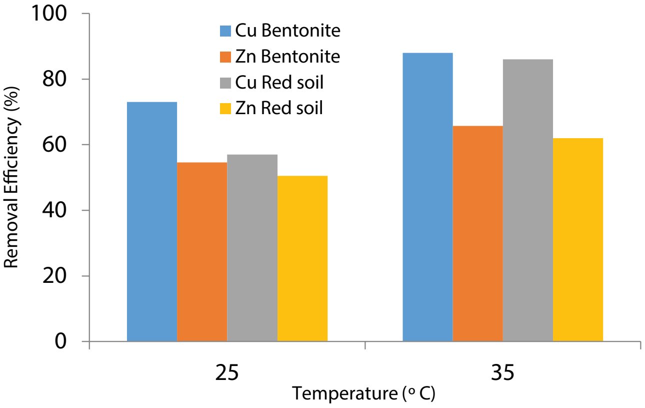


Fig. 8. Effects of temperature on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (initial concentration of metals = 50 mg/L, adsorbent concentration = 24 g/L, pH = 5, contact time = 100 min, particle size = 0.5–0.8 mm, mixing speed = 150 rpm).

Increasing the temperature from 25°C to 35°C increased the $Cu^{2+}$ and $Zn^{2+}$ removal efficiency using red soil and activated bentonite. As the temperature was increased, the removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ ions increased by red soil and activated bentonite. As the temperature was increased, the cations were adsorbed faster [51,52]. It seems that the process of adsorption of $Cu^{2+}$ and $Zn^{2+}$ ions by natural soils is a thermal reaction. The rate of adsorption increases when the temperature is increased because of the enlargement of the porous surface of the adsorbent and the penetration of particles into them [53]. It seems that the process of adsorption of $Cu^{2+}$ and $Zn^{2+}$ ions by natural soils is a thermal reaction. The results indicate that adsorption capacity and equilibrium increase with increasing temperatures [54]. Similar results have been reported in studies by Dho et al. [54] and Xing et al. [55].

### *3.7. Effects of initial concentration of metals on removal efficiency*

The effects of the initial concentration of metals on the adsorption of $Cu^{2+}$ and $Zn^{2+}$ from synthetic samples using activated bentonite and red soil adsorbents are shown in Fig. 9.

Due to the saturation of the exchange sites by adsorption, removal efficiency was decreased when the initial concentration of metals was increased.

When the metal concentration was increased, removal efficiency was decreased. When the concentration of metal ions was 10 mg/L, the removal efficiency rates for $Cu^{2+}$ and $Zn^{2+}$ by activated bentonite were 86% and 68%, and at a metal ion concentration of 100 mg/L, the removal efficiency rates were 28% and 24%, respectively. When the metal ion concentration was 10 mg/L, the removal efficiency rates for $Cu^{2+}$ and $Zn^{2+}$ by red soil were 84% and 67%, and at a metal ion concentration of 100 mg/L, the removal efficiency rates were 25% and 19%, respectively. The rapid adsorption rate at the initial stage may be described by an increased accessibility in the number of available sites on the adsorbent surface. The adsorption was normally controlled by the diffusion process from the mass to the surface. As time passes, adsorption sites become more inactive. The remaining vacant sites cannot easily be occupied by cations due to the repulsive forces between the adsorbate and the mass phase. Adsorption due to limited sites is probably a controlled process [56]. The adsorption of zinc metal ion is affected by the presence of copper metal ion. In a soil with a low cation exchange capacity, adsorbed Cu was not notably affected by added Zn, but the presence of Cu, at low concentration, completely barricaded Zn adsorption [49]. Similar results have been reported by Esmaeili et al. [16] and Melichova et al. [57].

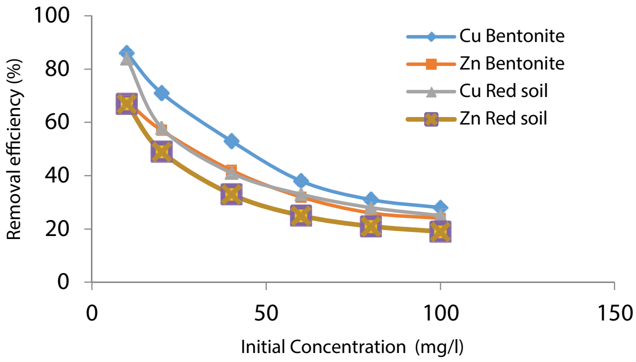


Fig. 9. Effects of initial concentration of metals on removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite from acid mine drainage from copper mining (temperature = 25°C, adsorbent concentration = 24 g/L, pH = 5, contact time = 100 min, particle size = 0.5–0.8 mm, mixing speed = 150 rpm).

### *3.8. Adsorption capacity*

The initial concentration of metals in solution and pH have an important role in heavy metal retention rate. When concentration increases and pH decreases, it can be concluded that the sorption coefficient for $Cu^{2+}$ and $Zn^{2+}$ reduces notably. As there are many metals in solution, there is an increase in the ionic competition between metals and $Cu^{2+}$ and $Zn^{2+}$ for superficial sites in adsorbents. The reduction in the adsorption efficiency of any metal can be due to the presence of a large amount of metal in the solution [58]. In the real sample, there were a lot of metals that competed with copper and zinc metal ions to absorb. The highest concentration is related to Mn (60 mg/L), Mg (99.5 mg/L), Si (23.5 mg/l), Na (21.5 mg/L), and Ca (79.5 mg/L). This was one of the reasons for the low adsorption of activated bentonite and red soil. Activated bentonite showed a higher adsorption rate than red soil. pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content have an important role in the adsorption of $Cu^{2+}$ and $Zn^{2+}$. Metal cations form complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ion and may be uncharged or carry a net negative charge. The type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH, and redox are effective on the formation of complexation. The mobility or melting of a metal in solution depends on the presence of complex ligands.

The double-faced interactive behavior of carbonates and $Cu^{2+}$ and $Zn^{2+}$ could be explained by the following reactions [59]:

$$\mathrm{CaCO}_{3(s)} \leftrightarrow \mathrm{Ca}^{2+}_{(\mathrm{aq})} + \mathrm{CO}^{2+}_{(\mathrm{aq})} \tag{9}$$

$$\mathrm{CO}^{2+}_{(\mathrm{aq})} + \mathrm{M}^{2+}_{(\mathrm{aq})} \leftrightarrow \mathrm{M\,CO}_{3(s)} \tag{10}$$

In addition, the ion exchange may also operate as a possible sorption mechanism as follows:

$$\mathrm{M}^{2+} + \mathrm{CaCO}_3 \leftrightarrow x\mathrm{Ca}^{2+} + \mathrm{M}\,y\,\mathrm{Ca}_{(1-x)}\mathrm{CO}_3 + (1-y)\mathrm{M}^{2+} \tag{11}$$

### *3.9. Determination of adsorption isotherms*

The Freundlich isotherm and Langmuir isotherm of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite are shown in Figs. 10(a) and (b), respectively.

In the Freundlich adsorption model, $K_F$ can be defined as the adsorption coefficient and also for a unit equilibrium concentration the number of cations adsorbed onto adsorbents. The slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity. A value for 1/*n* below one indicates a normal Freundlich isotherm, and 1/*n* above one is an indication of cooperative adsorption [46]. The values of 1/*n* obtained in this study were observed to be more than unity and had values of 1.41, 1.03 for $Cu^{2+}$ and 1.03, 1.02 for $Zn^{2+}$ metal ions, which indicate cooperative adsorption. The good fit of the experimental data and the correlation coefficients demonstrated the applicability of the Langmuir isotherm model. It is noteworthy that the values of the correlation coefficient ($R^2 \geq 0.98$) for the Langmuir isotherm model represent a considerable correlation [34]. The correlation coefficients of adsorption and constants of Langmuir and Freundlich isotherms indicated that the process of $Cu^{2+}$ and $Zn^{2+}$ adsorption onto activated bentonite and red soil showed both Langmuir isotherm and Freundlich adsorption models. Results indicated that Freundlich adsorption isotherm was the best model for the metal ion adsorption onto activated bentonite and red soil with higher $R^2$.

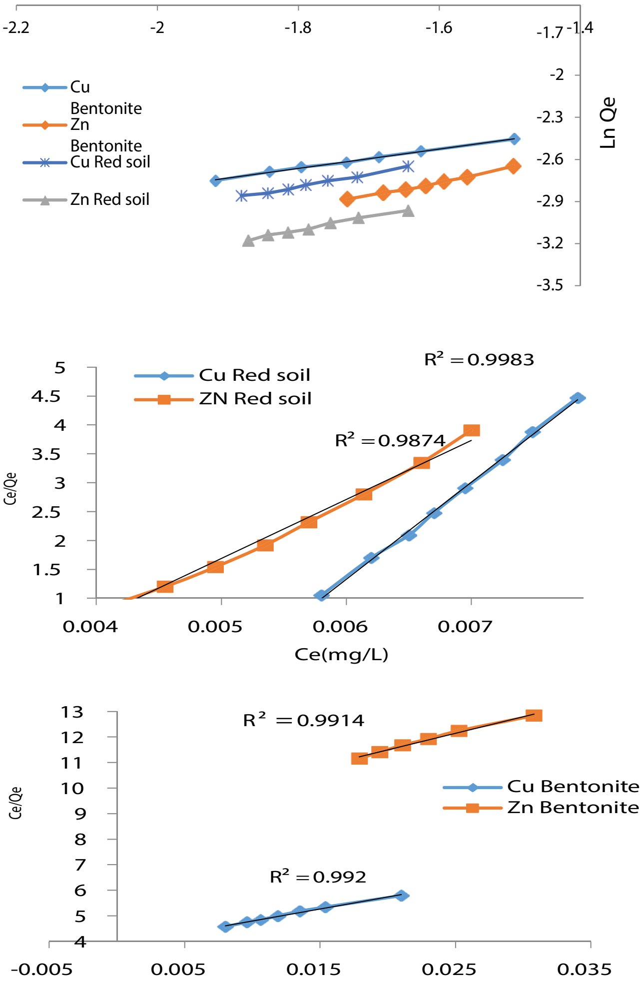


Fig. 10. (a) Freundlich isotherm for adsorption of $Cu^{2+}$ and $Zn^{2+}$ using red soil and activated bentonite and (b) Langmuir isotherm for adsorption of $Cu^{2+}$ and $Zn^{2+}$ on red soil and activated bentonite.

The balance information obtained from $Cu^{2+}$ and $Zn^{2+}$ adsorption by activated bentonite and red soil is shown in Table 4.

In this study, the two most widely used kinetic models, pseudo-first-order and pseudo-second-order models, were employed which are mentioned above. In the pseudo-first-order model, the rate constant $k_1$ and correlation coefficient, $R^2$, were determined by plotting $\log(q_e - q_t)$ against time, with $R^2$ in the range of 0.71–0.92 for various physicochemical parameters. By comparing the rate constants, it can be seen that no relationship can be found between different initial concentrations and also between different sorbents as the values are highly inconsistent and hence insignificant. As a rule, the pseudo-first-order model is suitable at very low concentrations, but in our case, the concentration of contaminant taken was 18–97.5 mg/L for $Zn^{2+}$ and $Cu^{2+}$ and the mass of the sorbent was 8–28 g. In the pseudo-second-order model for copper and zinc adsorption, the information in Table 5 indicates that the second-order rate constant varied from 503.6 to 1,899.3 g/mg/min. It was observed that the increase of initial concentrations was associated with a decrease in adsorption. The values of $k_2$ are consistent, $R^2$ values are high, and all these thermodynamic parameters presented in order kinetic model are fitted very well. With high initial concentrations, pseudo-second order gave better results than pseudo-first order.

### 3.10. Adsorption mechanism

In activated bentonite FTIR spectra analysis, the existence of two intense OH band at 3,625.8 and 3,427.39 cm$^{-1}$ is the reason for higher adsorption of $Cu^{2+}$ and $Zn^{2+}$. These results for the red soil were obtained at 3,616.67 and 3,424.14 cm$^{-1}$. OH groups function as an active site for the binding of positively charged cation [60].

Table 4
Parameters of the Langmuir and Freundlich adsorption isotherm models for the adsorption of $Cu^{2+}$ and $Zn^{2+}$ on activated bentonite and red soil

| Adsorbent | | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|---|
| | | $Q_0$ (mg/g) | *b* (L/mg) | $R^2$ | $K_f$ (mg/g) | 1/*n* (–) | $R^2$ |
| Activated bentonite | Zn | 4.6 | 0.4 | 0.99 | 4.16 | 1.03 | 0.991 |
| | Cu | 6.27 | 0.25 | 0.99 | 5.37 | 1.41 | 0.997 |
| | | $Q_0$ (mg/g) | *b* (L/mg) | $R^2$ | $K_f$ (mg/g) | 1/*n* (–) | $R^2$ |
| Red soil | Zn | 9.45 | 0.58 | 0.98 | 3.63 | 1.02 | 0.996 |
| | Cu | 5.32 | 0.49 | 0.99 | 3.80 | 1.03 | 0.99 |

Table 5
Comparison of the first-order and second-order adsorption rate constants for different initial copper and zinc concentrations with red soil and activated bentonite

| Parameters | | $Cu^{2+}$ | | | | Parameters | | $Zn^{2+}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Pseudo-first-order | | Pseudo-second-order | | | | Pseudo-first-order | | Pseudo-second-order | |
| Sorbent | Initial concentration (mg/L) | $k_1$ (1/min) | $R^2$ | $k_2$ (g/mg min) | $R^2$ | Sorbent | Initial concentration (mg/L) | $k_1$ (1/min) | $R^2$ | $k_2$ (g/mg min) | $R^2$ |
| Red soil | 10 | 0.359 | 0.929 | 1,859 | 0.951 | Red soil | 10 | 0.124 | 0.918 | 1,743 | 0.935 |
| | 20 | 0.693 | 0.801 | 721.600 | 0.941 | | 20 | 0.241 | 0.924 | 936.400 | 0.937 |
| | 30 | 0.818 | 0.817 | 625.300 | 0.943 | | 30 | 1.112 | 0.781 | 631.500 | 0.945 |
| | 40 | 0.521 | 0.931 | 592 | 0.943 | | 40 | 1.053 | 0.779 | 503.800 | 0.945 |
| Activated bentonite | 10 | 0.365 | 0.964 | 1,652 | 0.935 | Activated bentonite | 10 | 0.254 | 0.912 | 1,899.300 | 0.937 |
| | 20 | 0.312 | 0.889 | 1,098.400 | 0.943 | | 20 | 0.118 | 0.910 | 1,092 | 0.938 |
| | 30 | 0.293 | 0.935 | 691.700 | 0.942 | | 30 | 0.275 | 0.932 | 679 | 0.937 |
| | 40 | 0.298 | 0.952 | 523.800 | 0.942 | | 40 | 0.171 | 0.909 | 503.600 | 0.932 |

Table 6
Chemical composition of acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan

| Parameter | Max and min in AMD (mg/L) | Parameter | Max and min in AMD (mg/L) | Parameter | Max and min in AMD | Parameter | Max and min in AMD** (mg/L) |
|---|---|---|---|---|---|---|---|
| Na | 12–31 | Cu | 62–133 | Sb | 0.01–0.08 (mg/L) | $PO_4^{-3}$ | 0.9–1 |
| K | 1.6–5.3 | Zn | 11–25 | Ni | 0.7–3.6 (mg/L) | $NO_2$ | 8–12 |
| Mg | 43–156 | Pb | 0.007–0.015 | Se | 0.001–0.15 (mg/L) | $NO_3$ | 8–17 |
| Ca | 20–139 | Mn | 47–73 | As | 0.006–0.035 (mg/L) | $NO_2 + NO_3$ | 16–27 |
| AL | 0.01–0.03 | Mo | 0.001–0.025 | Si | 21–26 (mg/L) | $SO_4$ | 510–2,410 |
| Fe | 0.04–0.6 | Co | 0.2–0.65 | Cr | 0.01–0.06 (mg/L) | $HCO_3 + CO_3$ | 7–9.5 |
| Cd | 0.02–0.15 | Cl | 11–22.5 | pH | 5.4 | | |

**AMD: acid mine drainage

Commonly, there are two fundamental mechanisms for heavy metal adsorption: specific adsorption, which is described by more selective and less reversible reactions including chemisorbed inner-sphere complexes, and ion exchange, which involves rather weak and less selective outer-sphere complexes. Specific adsorption occurs slowly and takes about the strong and constant binding of $Cu^{2+}$ and $Zn^{2+}$ with the adsorbent. The ion exchange is reversible in nature and occurs rather quickly as it is typical for reactions that are diffusion controlled and of electrostatic nature. The adsorption of $Cu^{2+}$ and $Zn^{2+}$ ions on red soil and activated bentonite was rapid and reversible, indicating that the copper and zinc were mostly removed by cation exchange [55].

The removal of $Cu^{2+}$ and $Zn^{2+}$ ions can be attributed to cation exchange between cations and adsorbents:

$$2(\equiv SOH) + Me^{2+} \rightarrow \equiv (SO)_2\, Me^{2+}\, H^+$$

where S represents functional groups in red soil and activated bentonite.

### *3.11. Removal of $Cu^{2+}$ and $Zn^{2+}$ from real wastewater*

The results of the study of the chemical quality of acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan are shown in Table 7.

Experiments on the real sample showed that 88% of copper was removed using red soil and 76% by the application of activated bentonite. The comparison of the removal efficiency of $Zn^{2+}$ in real and synthetic samples shows a decrease in the real sample (66% and 79% in synthetic and 42% and 58% in the real sample using red soil and activated bentonite, respectively). The results showed that zinc had a limited chance in competing with other existing metal ions in the real sample. $Zn^{+}$ had a different removal efficiency in the single-metal system ($Zn^{2+}$) and in the presence of other metals like the real solution. In real samples, the combination of metal cations like $Cu^{2+}$ and $Zn^{2+}$ with organic and inorganic compounds occurred as the resulting compounds had less positive charge. These compounds also affect the mobility and deposition of metals.

Table 7
The removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ by red soil and activated bentonite from acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan under optimal conditions

| Metal<br>Adsorbent | Removal efficiency of $Cu^{+2}$ (%) | Removal efficiency of $Zn^{+2}$ (%) |
|---|---|---|
| Activated bentonite | 78 | 58 |
| Red soil | 86 | 42 |

According to the analysis in Table 6, the metals found in the highest amounts in the acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan are Cu, Mg, Mn, Zn, and Si in amounts of 62–133, 43–156, 36–58, 11–25, and 21–26 mg/L, respectively. Low levels of lead, iron, aluminum, nickel, selenium, and other metals were also observed. The results of the removal efficiency of $Cu^{2+}$ and $Zn^{2+}$ by red soil and activated bentonite from acid mine drainage from the Sarcheshmeh copper mine in Rafsanjan under optimal conditions are shown in Table 7.

Heavy metal adsorption behavior is greatly influenced by soil properties (clay minerals, iron oxides, soil organic matter in the beginning). Soil adsorption capacity is determined by the number and type of available binding sites. Since Cu adsorption is dependent on covalent interactions (internal complex) with soil components, Cu is absorbed more than Zn and is mainly maintained through electrostatic interactions. A metal that has a stronger bond to adsorption sites is less affected by metals that have a weaker bonding. Hereupon, Cu is mostly absorbed and the strongest competitor for metals and soil constituents in all conditions. The adsorption of heavy metals is considerably affected by the presence of large cations such as $Ca^{2+}$. $Ca^{2+}$ has a strong competition with metal ions on adsorption sites since Zn is mainly retained in the soil by exchange reactions but Cu forms inner-sphere complexes with soil constituents; this competition is greater for Zn than for Cu [61].

## 4. Conclusion

Red soil and activated bentonite adsorbed $Cu^{2+}$ with a higher efficiency than they adsorbed $Zn^{2+}$. Red soil adsorbed $Cu^{2+}$ more effectively and more efficiently compared with under similar conditions. The adsorption of heavy metals on red soil and bentonite followed the order of $Cu^{2+} > Zn^{2+}$ and were fitted to the Freundlich adsorption model. Kinetic models like pseudo-first order and second order proved that along with surface adsorption, chemisorption, desorption, and ion exchange are taking place. The conclusion has been made that sorption coefficient (amount adsorbed) decreased with increasing concentration. The current study showed that the adsorption of $Cu^{2+}$ from acid mine drainage from copper mining by red soil and activated bentonite is economical.

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## Symbols

$b$ — Correlation energy adsorption
$C_0$ — initial concentration of the metal solution
$C_e$ — equilibrium concentration in the metal solution
$K_F$ — Freundlich constant
LOI — Loss of ignition
$n$ — Freundlich constant
$Q°$ — maximum equilibrium adsorption capacity of metal on the surface of the adsorbent
$q_e$ — adsorption capacity of the adsorbent
$R$ (%) — removal percentage of metal on the adsorbent
$R^2$ — Regression coefficient
$V$ — Volume of the metal solution

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